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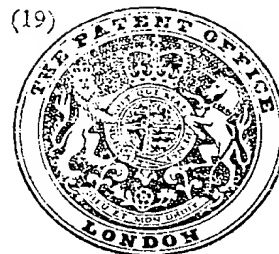
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(54) CATALYST SUPPORTS

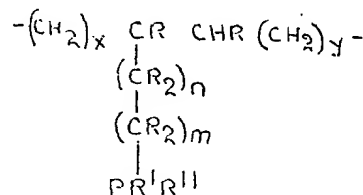
(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, EC2., a company incorporated in accordance with the Laws of England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to a catalyst support, to catalysts derived from the support and to processes for preparing them.

The use of phosphine complexes of transition metals as homogeneous catalysts for a variety of reactions such as carboxylation, hydrogenation and oligomerisation of olefins is known. These catalysts often contain valuable metals, for example palladium and iridium and catalyst recovery and recycle is therefore of great importance. However, it is often a problem to achieve a high degree of catalyst recovery.

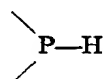
We have now discovered that special polymeric supports, themselves containing trivalent phosphorus groups, can be made which will form macromolecular transition metal complexes in many ways equivalent to the catalysts mentioned above, and which are easier to recover.

Thus according to one aspect of the present invention there is provided a polymeric catalyst support material containing from 0.1 to 20% by wt of phosphorus and containing units of the formula:



where the groups R, R¹ and R¹¹ are aryl groups or alkyl or cycloalkyl groups containing up to 6 carbon atoms, or hydrogen, and x, y, n and m are 0 or an integer up to 3 with the proviso that x, y, m and n do not all have integral values greater than 1 and p is an integer, the molecular weight of the polymeric material being greater than 1000.

According to another aspect of the present invention there is provided a process for the production of a catalyst support material as hereinbefore defined comprising reacting an olefinically unsaturated polymer of molecular weight at least 300 and having a bromine number of at least 0.5 at a temperature in the range from room temperature to 250°C with a compound containing trivalent phosphorus and containing at least one



bond under conditions such that the phosphorus-containing compound adds to the double bonds of the polymer.

[Price 25p]

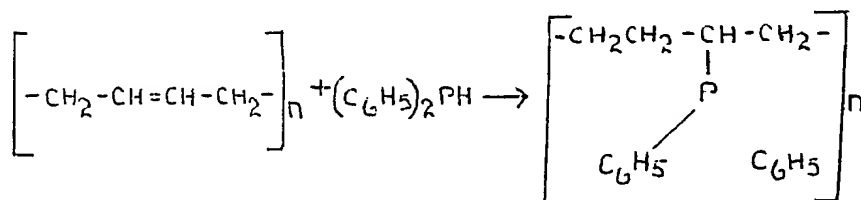
Preferably the unsaturated polymer has a molecular weight in the range 300 to half a million, although higher molecular weight materials can be used.

Suitable olefinically unsaturated polymers are polymers of dienes, particularly conjugated dienes e.g. polybutadiene, polychloroprene, poly 1:3 pentadiene and polyisoprene. It has been found that it is easier to get phosphorus into 1:2 polybutadiene than 1:4 polybutadiene and the former is therefore preferred. Also suitable are polymers prepared by the dehydrohalogenation of polyvinyl chloride or dehydration of polyvinyl alcohol.

Graft, random, alternate or block copolymers of dienes with other monomers e.g. styrene can be used. Typical copolymers are butadiene/styrene.

Suitable phosphorus compounds are alkyl, cycloalkyl or aryl phosphines, or phosphine (PH_3) and particularly dialkyl, dicycloalkyl or diaryl phosphines. Phenyl phosphine, diphenyl phosphine, dicyclohexyl phosphine, diethyl, dipropyl, di butyl and dihexyl phosphines are preferred.

It is thought that the reaction proceeds as follows in a typical case:—



The reaction can be simply performed by stirring the polymers in the phosphorus-containing compound under an inert atmosphere such as dry nitrogen with a solvent if necessary. A free radical initiator such as ultra-violet light, a peroxide such as t-butyl hydroperoxide or an azo compound such as α,α' azo bis isobutyronitrile is added and the mixture is heated over a period as necessary. The amount of heating and the time for which it is required will usually depend chiefly on the characteristics of the initiator chosen and particularly its half life, which varies with temperature.

The phosphorus-containing support material preferably contains from 0.1 to 15% by wt. of phosphorus.

Any suitable inert organic solvent such as cyclohexane may be used.

The olefinically unsaturated polymer is usually mixed with a stoichiometric excess of the phosphorus-containing compound. It has been found convenient to use the phosphorus containing compound as a solvent for the polymer.

These polymers may be reacted with a number of transition metal compounds to give macromolecular transition metal complexes which can be in many ways equivalent to the catalysts mentioned above, and which are generally easier to recover. These compositions may also be useful as heat and flame resistant materials or as pigmented materials.

Thus according to another aspect of the present invention there is provided a catalyst which comprises a catalyst support material as hereinbefore defined, wherein the phosphorus atoms are bonded to transition metal atoms, to the extent that the catalyst contains from 0.01 to 20% by wt of metal.

Preferred transition metals are Group VIII metals although Cr, Mo, Mn, W, Re, Ti, V, Cu, and Au may also be used. Suitable Group VIII metal compounds are those capable of reacting with phosphines or substituted phosphines. Examples are halides such as the chlorides of formula RhCl_3 , MCl_2 (where M is a divalent Ni, Pd, Pt, or Co), Na_2PdCl_4 , IrCl_3 , TiCl_3 , CrCl_3 , ethylene complexes of iridium, palladium or platinum halides or carboxylates, π -allyl compounds such as π -allyl nickel chloride or its complexes with aluminium, alkyl, olefin cyclopentadienyl or π aromatic complexes.

Also suitable are metal carbonyls and carbonyl-containing metal complexes e.g. $\text{Ni}(\text{CO})_4$, $\text{Co}_2(\text{CO})_8$, $\text{Rh}(\text{CO})_2$ acetyl acetonate, $\text{Fe}(\text{CO})_5$, $\text{Mn}_2(\text{CO})_{10}$, $\text{M}(\text{CO})_6$ where M is Cr, Mo or W, $\text{V}(\text{CO})_6$, $\text{Rh}_2(\text{CO})_{12}$, Cl_2 and $\text{RCO Co}(\text{CO})_4$ where R is an alkyl or aryl group.

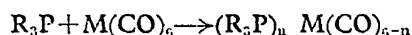
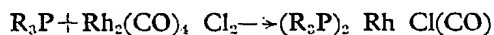
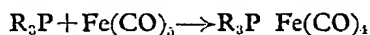
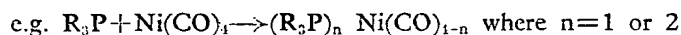
The catalyst compositions containing transition metal are prepared at temperatures in the range -20 to 250°C under conditions such that the transition metal atoms become bonded to the phosphorus atoms. The reaction is often effected by warming the transition metal compound and the phosphorus-containing support in a suitable solvent for one or both of the reactants. In some cases it will be desirable to perform

the reaction at room temperature or below. Saturated or aromatic hydrocarbons, halogenated hydrocarbons, alcohols, ethers or mixtures of these may be used as solvents.

Heating will usually be carried on for $\frac{1}{2}$ to 6 hours but the reaction time may be longer or shorter in specific instances.

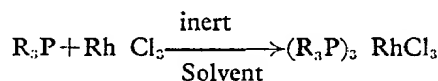
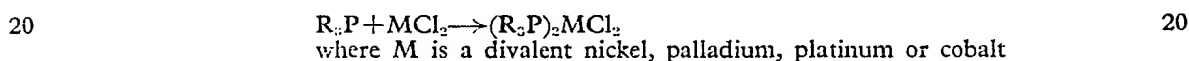
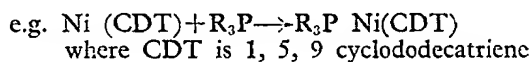
5 In the formation of the metal-containing polymer it often occurs that one of the following reactions takes place:— 5

(a) the transition metal compound contains a displaceable ligand such as carbonyl, olefin, diolefin, phosphine or a solvent molecule e.g. tetrahydrofuran, and the ligand is displaced under the reaction conditions whilst the transition metal atom chelates 10 with the phosphorus 10

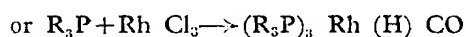
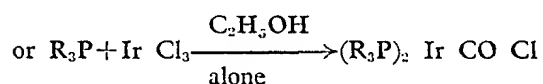
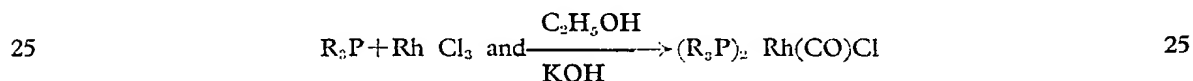


15 where $M=Cr, Mo$ or W , $n=1$ or 2 . 15

(b) the transition metal is capable of increasing its co-ordination number under the reaction conditions and thereby permits the chelate to be formed.



(c) The reaction takes place in the presence of a solvent which enters into the reaction e.g. C_2H_5OH admixed with KOH which introduces as CO groups as in



effected either in $HCHO$ in ethanol or $NaBH_4$ in ethanol.

In the above formula at least one of the R groups will be a polymer chain while the others may be alkyl or aryl. 30

Many of the compositions of this invention are active as catalysts and are similar to such homogeneous phosphine-containing complexes as $IrH_3(Ph_3P)_3$ or $IrH_2(OOCCH_3)(Ph_3P)_3$ for the hydrogenation of aldehydes or $PdCl_2(Bu_3P)_2$ for the carboxylation of olefins.

35 A co-catalyst such as an aluminium alkyl, aluminium alkyl halide or aluminium trihalide or sodium borohydride may be necessary to render the phosphine containing complex active. 35

A number of catalyst systems consist of a mixture of transition metal compound, a phosphine and a reducing agent, such as an aluminium alkyl. Examples are:—

40 $M(acac)_n + Ph_3P + Et_3Al(OEt)$ for the cyclodimerisation of butadiene where M is $Fe(III)$, $Co(III)$ or $Ni(II)$, n is 2 or 3 and $acac$ is acetylacetonate. 40

$Ni(acac)_2 + R_3P + Et_3Al_2Cl_3$ for propylene oligomerisation and $(RCOO)_2Ni + Ph_3P + R_2AlCl$ for propylene dimerisation. The active species in these cases is formed in situ.

45 The phosphine compounds in this case may be replaced by the phosphorus- 45

containing polymers of the present invention forming the active species on the polymer surface and providing a catalyst which utilizes a composition according to the present invention.

5 The polymeric support materials of the present invention can in certain cases, also be used as heat and flame retardent materials for example flame retardant polybutadiene and polyisoprene, lubricating oil additives (where solubility permits) and sequestering agents for transition metals in solution. 5

The invention is illustrated by the following examples.

Example 1

10 In Examples 1 to 3 the polybutadiene was 98% cis and had a molecular weight above 30,000 and was prepared using a titanium-aluminium Ziegler catalyst. 10

2.7 g of polybutadiene were placed in a silica flask under nitrogen 40 ml (approximately 0.2 moles) of diphenyl phosphine were added under nitrogen and the reaction mixture stirred until the polymer dissolved. The flask was then irradiated with UV 15 light for 24 hours with stirring. The excess diphenyl phosphine was vacuum distilled from the reaction mixture and the resulting polymer dissolved in 150 ml of toluene and precipitated with methanol. The polymer was then evacuated. Phosphorus content=1.7 per cent weight. 15

Example 2

20 2.7 g of polybutadiene were placed in a flask under nitrogen and 20 ml of diphenyl phosphine (approximately 0.1 moles) added. The reaction mixture was stirred until the polymer dissolved and then 10 drops of tertiary-butyl hydroperoxide were added. The reaction mixture was refluxed at 140°C for 6 hours and then treated as described above. Phosphorus content=2.0 per cent weight. 20

Example 3

25 5.4 g of polybutadiene were dissolved in 200 ml of cyclohexane under nitrogen. 19 ml (0.1 moles) of diphenyl phosphine dissolved in 50 ml of cyclohexane were added followed by 5 g of α,α' azo bis isobutyronitrile. The reaction mixture was heated at 80°C for 12 hours and irradiated with UV light. The polymer was recovered by precipitation with methanol and then evacuated. Phosphorus content=0.9 per cent weight. 25

Example 4

35 2.5 g of 1,2-polybutadiene were placed in a silica flask under nitrogen and 50 ml of diphenyl phosphine added. The reaction mixture was shaken mechanically until the polymer had dissolved and then irradiated with UV light for 72 hours at room temperature under nitrogen. The excess diphenyl phosphine was then evaporated off. The resulting polymer was dissolved in 15 ml of toluene and then precipitated from solution with 300 ml of *n*-hexane. This procedure was repeated 5 times. Finally the polymer was dissolved into 50 ml of toluene, the toluene evaporated off and the polymer dried in vacuo at 120°C for 12 hours. 35

The polybutadiene was 88% 1:2 4% trans 1:4 8% cis 1:4 and had a M.W of 28,000 and was prepared by anionic polymerisation in tetrahydrofuran. 40

Phosphorus content=7.9 per cent weight.

Example 5

45 1 g of the phosphorus-containing polymer (prepared as in Example 4) was dissolved in 50 ml of toluene and 0.26 g of anhydrous cobalt (II) chloride in 10 ml of *n*-butanol added. The reaction mixture was refluxed under nitrogen for 2 hours. A blue polymeric material precipitated. This was extracted briefly with a 10 per cent v/v solution of *n*-butanol in toluene. The polymer was then heated in 300 ml of refluxing *n*-butanol and the resulting solution cooled and poured into 1 litre of pentane. 50 The polymer was filtered off, washed with pentane and dried in vacuo. 50

Cobalt content=3.1 per cent weight.

Example 6

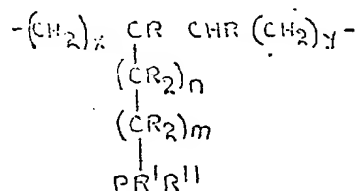
55 5 g of 1,2-polybutadiene as used in Example 4 were placed in a silica flask under nitrogen and 50 ml of di-*n*-hexyl phosphine added. The reaction mixture was shaken mechanically until the polymer had dissolved and then irradiated with UV light for 72 hours at room temperature under nitrogen. The excess of di-*n*-hexyl phosphine was evaporated off at 200°C under a vacuum of 0.5 mm Hg. The polymer was then redissolved in 25 ml of degassed toluene and precipitated with 400 ml of deaerated 55

methanol. This procedure was repeated 5 times. The polymer was finally redissolved in 100 ml of degassed toluene; the toluene evaporated off and the polymer dried at 120°C for 12 hours in vacuo.

Phosphorus content=11.2 per cent weight

5 WHAT WE CLAIM IS:—

1. A polymeric catalyst support material containing from 0.1 to 20% by wt of phosphorus and containing units of the formula:



10 where the groups R, R¹ and R¹¹ are aryl groups or alkyl or cycloalkyl groups containing up to 6 carbon atoms, or hydrogen, and x, y, n and m are 0 or an integer up to 3 with the proviso that x, y, m and n do not all have integral values greater than 1 and p is an integer, the molecular weight of the polymeric material being greater than 1000.

15 2. A polymeric catalyst support material as claimed in claim 1 wherein x is 0, y is 0 and m and n are each 1.

3. A polymeric catalyst support material as claimed in claim 1 wherein m is 0, n is 0, x is 2 and y is 0.

20 4. A polymeric catalyst support material as claimed in any of claims 1 to 3 having a molecular weight of greater than 5,000.

5. A process for the preparation of a catalyst support material as claimed in claim 1 comprising reacting an olefinically unsaturated polymer of molecular weight at least 300 and having a bromine number of at least 0.5 at a temperature in the range from room temperature to 250°C with a compound containing trivalent phosphorus and containing at least one



bond under conditions such that the phosphorus-containing compound adds to the double bonds of the polymer.

6. A process as claimed in claim 5 wherein the compound containing trivalent phosphorus is of the formula



where R¹ and R¹¹ are the same or different aryl or alkyl groups containing up to 6 carbon atoms per molecule, or hydrogen atoms.

35 7. A process as claimed in claim 6 wherein the compound containing trivalent phosphorus is selected from phenyl, diphenyl, dicyclohexyl, diethyl, dipropyl, dibutyl and di n hexyl phosphines.

8. A process as claimed in any one of the preceding claims wherein the olefinically unsaturated polymer is a polymer of a diene.

9. A process as claimed in claim 8 wherein the olefinically unsaturated polymer is a polybutadiene or polyisoprene.

40 10. A catalyst comprising a polymeric support material as claimed in any one of claims 1 to 4, wherein phosphorus atoms are bonded to the transition metal atoms to the extent that the catalyst contains 0.01 to 20% by wt of metal.

11. A catalyst as claimed in claim 10 wherein the metal is a Group VIII metal.

12. A process for the preparation of a catalyst material containing from 0.01

to 20% by wt of a transition metal which comprises reacting (a) a compound of the transition metal with (b) a catalyst support material as claimed in any of claims 1 to 4, at a temperature from -20 to 250°C under conditions such that the transition metal atoms become bonded to the phosphorus atoms.

5 13. A process as claimed in claim 12 wherein the transition metal compound contains a ligand which is displaced under the reaction conditions. 5

14. A process as claimed in claim 12 wherein the transition metal compound increases its co-ordination number under the reaction conditions.

10 15. A process as claimed in claim 12 wherein the reaction is effected in the presence of a solvent for the transition metal compound and the solvent takes part in the reaction. 10

16. A process for the preparation of catalyst support materials substantially as hereinbefore described with reference to any one of Examples 1 to 4 or 6.

15 17. A process for the preparation of a catalyst material substantially as hereinbefore described with reference to Example 5. 15

18. Catalyst support materials whenever prepared by a process as claimed in any of claims 5 to 9 or 16.

19. Catalyst materials whenever prepared by a process as claimed in any of claims 12 to 15 or 17.

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